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Chapter 4

4.1 Moving Boundary Work

Moving Boundary Work (Boundary Work): the work associated with the expansion or compression of a gas generally in a piston-cylinder device

For this section, it is a quasi-equilibrium process

$$W_b = \int_1^2 P d\mathcal{V}$$

- \therefore Boundary work is negative for compression and positive for expansion
- This equation also proves that the area under the process curve on a P - \mathcal{V} diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression of a closed system
- In a more realistic system the equation expands to:

$$W_b = W_{\text{friction}} + W_{\text{atm}} + W_{\text{crank}} = \int_1^2 (F_{\text{friction}} + P_{\text{atm}}A + F_{\text{crank}})dx$$

Polytropic Process: during actual expansion and compression process P and \mathcal{V} are related by

$$P = C\mathcal{V}^{-n} \text{ (where } C \text{ and } n \text{ are constants)}$$

This is called a polytropic process and can be used to find boundary work with,

$$W_b = \int_1^2 P d\mathcal{V} = \int_1^2 C\mathcal{V}^{-1} d\mathcal{V} = P\mathcal{V} \ln\left(\frac{\mathcal{V}_2}{\mathcal{V}_1}\right)$$

4.2 Energy Balance for Closed Systems

Energy Balance:

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

- Per unit mass

$$e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}}$$

- For a cycle

$$W_{\text{net,out}} = Q_{\text{net,in}}$$

- Therefore, for a closed system

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}}$$

- Note: Q_{in} and W_{out} are positive and Q_{out} and W_{in} are negative

4.3 Specific Heats

Specific Heat: the energy required to raise the temperature of the unit mass of a substance by one degree

- Specific Heat at Constant Volume: the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant
 - Related to changes in the internal energy

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

- Specific Heat at Constant Pressure: the energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant
 - Related to changes in the enthalpy

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

4.4 Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

Using ideal gas law, definition of enthalpy, and the previous equations:

$$du = c_v(T) dT$$

$$dh = c_p(T) dT$$

Which lead to:

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT$$

Which can't be done easily by hand but can be approximated by:

$$u_2 - u_1 = c_{v,avg}(T_2 - T_1)$$

$$h_2 - h_1 = c_{p,avg}(T_2 - T_1)$$

Summary, one can determine the internal energy and enthalpy of ideal gases:

1. By using the tabulated u and h data
2. By using the c_v or c_p relations as a function of temperature and performing the integrations
3. By using average specific heats

Chapter 5

5.1 Conservation of Mass 214

Closed systems use the principle of conservation of mass because the mass remains constant, however, control volumes allow mass to cross the boundary so mass needs to be kept track of.

Mass Flow Rate: amount of mass flowing through a cross section per unit of time

- The differential mass flow rate is found with $\delta\dot{m} = \rho V_n dA_c$

The differential form is not always useful, so we like to use the average value while requires the average velocity:

$$V_{avg} = \frac{1}{A_c} \int_{A_{cn}^V} dA_c$$

Which gets us the following equation,

$$\dot{m} = \rho V_{avg} A_c$$

From this we can also get volume flow rate,

$$\dot{V} = \int_{A_{cn}^V} dA_c = V_{avg} A_c = V A_c$$

Which relates to mass flow rate,

$$\dot{m} = \rho \dot{V} = \frac{\dot{V}}{V}$$

Conservation of Mass: Net mass transfer in a control volume during a time interval.

Mass Balance Equations:

$$m_{in} - m_{out} = \Delta m_{cv}$$

Or,

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm_{cv}}{dt}$$

In a steady flow the total rate of mass entering a control volume is equal to the total rate of mass leaving the control volume.

$$\sum_{in} \dot{m} = \sum_{out} \dot{m}$$

This gets us the following equation,

$$\rho_1 V_1 A_1 = \rho_2 V_2 A_2$$

A special case occurs in incompressible flow since the density is constant which means the volume flow rate is constant, this gets us:

$$V_1 A_1 = V_2 A_2$$

5.2 Flow Work and the Energy of a Flowing Fluid 221

Flow Work/Flow Energy: Work needed to push the mass into or out of a flow volume.

$$W_{flow} = FL = PAL = PV$$

Dividing by mass gets us,

$$w_{flow} = Pv$$

Force of Fluid: $F = PA$

The total energy of a flowing fluid is,

$$\theta = Pv + e = Pv + (u + ke + pe)$$

After substituting in enthalpy, it becomes,

$$\theta = h + ke + pe = h + \frac{V^2}{2} + gz$$

Energy Transport:

$$E_{mass} = m\theta = m\left(h + \frac{V^2}{2} + gz\right)$$

Rate of Energy Transport

$$E_{mass}^{\cdot} = \dot{m}\theta = \dot{m}\left(h + \frac{V^2}{2} + gz\right)$$

5.3 Energy Analysis of Steady-Flow Systems 225

Steady-Flow Process: A control volume that has a process which allows for fluid to flow steadily

- Properties may change from point-to-point but at those points they do not change with time
- The intensive and extensive properties do not change with time
- The heat and work interactions with the surroundings do not change with time

Energy Balance of a steady-flow process,

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{system}}{dt} = 0$$

After substituting, this can be turned into,

$$\dot{Q}_{in} + \dot{W}_{in} + \sum_{in} \dot{m}\theta = \dot{Q}_{out} + \dot{W}_{out} + \sum_{out} \dot{m}\theta$$

For single-stream devices, this equation can be rearranged into,

$$q - w = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$$

Various Terms:

- \dot{Q} - Rate of heat transfer between control volume and surroundings
- \dot{W} - power
- Δh - change in enthalpy
- Δke - change in kinetic energy
- Δpe - change in potential energy

5.4 Some Steady-Flow Engineering Devices 228

Nozzle: Increase the velocity of a fluid by decreasing pressure

- Decreasing cross-sectional area

Diffuser: Increase pressure of a fluid by slowing it down

- Increasing cross-sectional area

Both nozzles and diffusers usually have a small rate of heat transfer rate, typically involve no work, and have negligible changes in potential energy.

However, changes in kinetic energy are not negligible.

Turbines produce work because of the fluid flowing through them.

- Negligible heat transfer and changes in potential energy

Compressors, pumps, and fans are used to increase the pressure of a fluid.

- Need to be supplied with work
- Negligible heat transfer, changes in potential energy, and changes in kinetic energy

Throttling Valve: Any type of flow restricting device that causes a large pressure drop of the fluid

- Accompanied by a large drop in temperature.
- Negligible work, heat transfer, change in potential energy, and change in kinetic energy
- This leaves enthalpy

Mixing Chamber: A chamber where mixing takes place

- Sum of inputted mass must equal sum of mass being output.
- Negligible work, heat transfer (if well insulated), change in potential energy, and change in kinetic energy

Heat Exchangers: Two moving fluids can exchange heat without mixing.

- Under steady operation the mass flow rate of each fluid remains constant
- Negligible work, change in potential energy, and change in kinetic energy
 - The external heat transfer is negligible if well insulated (not internal!)

Pipe and Duct Flow: Flow through a pipe

- Can involve heating sections or fans inside the pipe

5.5 Energy Analysis of Unsteady Flow Processes 242

Unsteady Flow/Transient Flow: When the flow changes within the control volume over time.

- Cannot use the steady-flow relations for this case
- Like a closed system but mass is not constant during the process and may involve moving boundaries with cause boundary work.

Unsteady Flow Mass Balance:

$$m_{in} - m_{out} = \Delta m_{system} = (m_2 - m_1)_{cv}$$

Unsteady Flow Energy Balance:

$$E_{in} - E_{out} = \Delta E_{system}$$

Uniform Flow Process: The fluid flow at the inlet and exit are uniform and steady and so the properties do not change with time, and if they do, they can be averaged.

- Approximation made for unsteady flow.

$$\left(Q_{in} + W_{in} + \sum_{in}^m \theta \right) - \left(Q_{out} + W_{out} + \sum_{out}^m \theta \right) = (m_2 e_2 - m_1 e_1)_{system}$$

With,

$$e = u + ke + pe$$

If kinetic energy and potential energy are negligible,

$$Q - W = \sum_{out}^m h - \sum_{in}^m h + (m_2 u_2 - m_1 u_1)_{system}$$

Chapter 6

6.1 Intro to the Second Law 276

The first law does not dictate the direction that a process will take place in or whether that process can occur in nature, this is where the second law of thermodynamics comes in.

- A process must satisfy both laws
- This violation is detected using the property called “entropy”

The second law is not limited to determining the direction of a process, it also states that energy has a quality and a quantity.

The second law also can be used to find the theoretical limits of common engineering systems as well as the degree completion.

- Defines perfection of thermodynamic processes

6.2 Thermal Energy Reservoirs 277

Thermal Energy Capacity: How much a material can supply or absorb finite amounts of heat without changing temperature.

Thermal Energy Reservoir: An object with a large thermal energy capacitance

- Oceans, lakes, and the atmosphere are good examples

- Any body that is large compared to the amount of energy being supplied can be modeled as a reservoir.

A two-phase system can be modeled as a reservoir since it can absorb and release large amounts of heat.

Source: Supplies energy in the form of heat

Sink: Absorbs energy in the form of heat

Heat Reservoirs: Another term for a thermal energy reservoir that absorbs and supplies heat.

6.3 Heat Engines 278

Heat Engines: A device which converts heat to work

- A great example being a steam power plant

Heat Engines are characterized by,

1. Receive heat from a high temperature source
2. Convert part of that heat to work
3. Reject remaining waste heat to a low temperature sink
4. Repeat on a cycle

Working Fluid: The fluid which is used to transfer the heat

Net Work Output of a Power Plant:

$$W_{net,out} = W_{out} - W_{in}$$

Can also be in terms of heat transfer alone,

$$W_{net,out} = Q_{out} - Q_{in}$$

Thermal Efficiency: The fraction of the heat input that is converted to net work output which is used to measure the performance of the heat engine.

Thermal Efficiency is,

$$\eta_{th} = \frac{(\text{Net Work Output})}{(\text{Total Heat Input})} = \frac{W_{net,out}}{Q_{in}}$$

It can also be written as,

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

Since heat engines involve a high temp reservoir and a low temp reservoir, the equation can be used to determine direction with,

$$\eta_{th} = \frac{W_{net,out}}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

Every heat engine must have some amount of waste energy by transferring it to a low temperature reservoir.

Kelvin-Planck Statement: It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

- Must have a low-temperature sink and a high temperature source to keep operating.
- Cannot have a thermal efficiency of 100 percent and this is a limitation that applies to both the idealized and actual heat engines

6.4 Refrigerators and Heat Pumps 283

Refrigerators: A device which transfers heat from a low-temperature medium to a high temperature medium.

Refrigerant: The working fluid in a refrigeration cycle.

Components and Steps of the Vapor-Compression Cycle:

1. Compressor – Compresses and increases the temperature of the refrigerant
2. Condenser – Cools down and condenses by releasing heat into the surrounding medium
3. Expansion Valve – Pressure and temperature drop dramatically due to throttling effect
4. Evaporator – Evaporates by absorbing heat from the refrigerated space.

Coefficient of Performance of a Refrigerator: A measure of the efficiency of the refrigerator.

$$COP_R = \frac{\text{Desired Output}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}}$$

Which can be rearranged into,

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

The coefficient of performance can be greater than one, unlike thermal efficiency.

Heat Pumps: Also transfers heat from a low-temperature medium to a high-temperature medium.

- Works on the same cycle as refrigerators but with a different objective.
- Used to maintain a heated space at a high temperature.

Coefficient of Performance of a Heat Pump: A measure of the efficiency of a heat pump.

$$COP_{HP} = \frac{\text{Desired Output}}{\text{Required Input}} = \frac{Q_H}{W_{net,in}}$$

Which can be rearranged into,

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

The relationship between the coefficient of performance of a heat pump and a refrigerator is,

$$COP_{HP} = COP_R + 1$$

Air conditioners are essentially refrigerators for a building or home.

Energy Efficiency Ratio: Measure of instantaneous energy efficiency defined by the ration of the rate of heat removal to the energy consumption

$$EER = 3.412COP_R$$

EER and COP of a refrigerator decrease with decreasing refrigeration temperature.

Clausius Statement: It is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher temperature body.

6.5 Perpetual Motion Machines 290

Perpetual Motion Machine of the First Kind: A device which violates the first law of thermodynamics.

- It would violate the first law by creating energy.

Perpetual Motion Machine of the Second Kind: A device which violates the second law of thermodynamics.

- An engine can't do work without an energy source, nor can it receive energy and convert it completely to work (efficiency cannot be 100%).

6.6 Reversible and Irreversible Processes 292

Reversible Process: A process which can be reversed without leaving any trace on the surroundings.

- This is only possible if the net heat and net work exchange between the system and the surroundings is zero.
- Merely an idealization, doesn't occur in nature
- Can be viewed as the theoretical limits for irreversible processes

Irreversible Process: A process which is not reversible.

Second Law Efficiency: Degree of approximation to the corresponding reversible process.

Irreversibilities: Factors that cause a process to be irreversible

Examples of Irreversibilities:

1. Friction – Requires work to overcome friction which is converted to heat which isn't undone when the process is reversed meaning the surroundings can't be resorted
2. Unrestrained Expansion of a Gas – Would need to compress the gas to its original volume and transfer heat until it returns to its original temperature, which would violate the second law.
3. Heat Transfer – Can only occur when there is a temperature difference between the system and the surroundings which makes it impossible for it to be reversible, but it can be minimized by decreasing the temperature difference.

Internally Reversible: No irreversibilities occur within the boundaries of a system

Externally Reversible: No irreversibilities occur outside the boundaries of a system

Totally Reversible: No irreversibilities occur within or outside the boundaries of a system

- Involves no heat transfer through a finite temperature difference, no nonquasi-equilibrium changes, and no friction

6.7 The Carnot Cycle 295

The Carnot cycle is a theoretical heat engine cycle which consists of four reversible processes. It is not physically possible to create a Carnot engine, but it is a process that represents a good first approximation for real, irreversible cycles and having a good understanding of the Carnot cycle can be applied to making more efficient engines.

A Carnot engine is a closed system with gas in a cylinder and a piston that moves frictionless inside the cylinder to compress the gas. The cylinder head (the circular end of the container opposite the piston) alternates between insulated and not. There is a thermal energy sink or source on the other side of the cylinder head, depending on the stage of the cycle. The four stages of the cycle are as follows:

1. Isothermal Expansion – The gas is at temperature T_H and is allowed to expand which moves the piston. As the gas expands, it maintains constant temperature because the energy source adds heat to maintain T_H . Since T_H is constant, this is a reversible process. The heat added is Q_H .
2. Adiabatic Expansion – The gas cools from T_H to T_L as it expands further. This pushes the piston more and increases the volume in the cylinder to maximum. Since it is frictionless, this is reversible. The cylinder head is also insulated, so no energy is transferred out of the gas.
3. Isothermal Compression – The piston is moved to compress the gas, and heat is transferred to the sink to keep the gas at T_L . This is just the opposite of process 1. The heat lost to the sink is Q_L .
4. Adiabatic Compression – The piston compresses the gas further, but the cylinder is no insulated. This raises the gas temperature to T_H .

The net work of the cycle is the area of the P-v curve for this reversible process and is determined by the difference between the work done by the gas to moving the piston (1-2 and 2-3) vs. the work done by the piston (3-4 and 4-1).

6.8 The Carnot Principles 297

The second law of thermodynamics leads to two conclusions for reversible and irreversible heat cycles. A heat engine cannot operate by exchanging heat with a single reservoir, and a refrigerator cannot operate without a net energy input from an external source. These conclusions are summed up by the Carnot Principles:

1. *The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.*
2. *The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.*

The book provides two visual proofs for these statements, and examples of engines which would be violations of these principles.

6.9 The Thermodynamic Temperature Scale 299

A thermodynamic temperature scale is a scale which is independent of the properties of the measurement tools. The Kelvin scale is a thermodynamic temperature scale. The second Carnot principle is the basis for the need for an independent scale. The efficiency of a reversible engine is just a function of T_H and T_L .

$$\eta_{th,rev} = 1 - \frac{Q_L}{Q_H} = f(T_H, T_L)$$

Which could be represented as

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

Since many functions satisfy the second law for a reversible process, Lord Kelvin proposed that the functions of temperature just be the temperature itself, so the relation between heat and temperature would become:

$$\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_L}$$

This ratio gives the representation of the Kelvin scale, and the magnitude of a kelvin is defined as 1/273.16 of the temperature interval between absolute zero and the triple-point temperature of water.

6.10 The Carnot Heat Engine 301

The efficiency of a Carnot engine is the reversible form of the thermal efficiency of any heat engine:

$$\eta_{th} = 1 - \frac{T_L}{T_H}$$

This is the best possible efficiency for a heat engine between two energy reservoirs. To maximize this value, the highest T_H and the lowest T_L values possible are desired.

A conclusion can be reached that energy has quality, and that higher temperature thermal energy has higher quality since the work output increases as the energy source temperature increases.

An example of quantity (first law) vs quality (second law) of energy is with dieting. Keeping track of daily calorie intake is the quantity, where the nutritional value of food being eaten is the quality.

6.11 The Carnot Refrigerator and Heat Pump 304

The Carnot cycle can be reversed to be used as a refrigerator or a heat pump. The coefficient of performance of a Carnot refrigerator is given as

$$COP_R = \frac{1}{Q_H/Q_L - 1} \quad \text{and} \quad COP_{R,rev} = \frac{1}{T_H/T_L - 1}$$

and the heat pump COR is given as

$$COP_{HP} = \frac{1}{1 - Q_L/Q_H} \quad \text{and} \quad COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

where the reversible equations give the maximum theoretical values. The value decreases as T_L decreases, so more work is needed to lower the temperature of the sink. As T_L approaches absolute zero, the work needed approaches infinity.

Chapter 7

7.1 Entropy 330

Irreversible processes are always less efficient than reversible processes, and comparing irreversible efficiencies to the equations for reversible efficiencies leads to inequalities. Clausius defined an inequality which is true for all processes, called the Clausius Inequality:

$$\oint \frac{\delta Q}{T} \leq 0$$

It is equal to zero for internally reversible processes and less than zero for an irreversible process. Clausius also found that the cyclic integral of any other property in a reversible cycle is zero, so the quantity $(\delta Q/T)_{int rev}$ must be a property as well. He defined this as entropy.

$$dS = \left(\frac{\delta Q}{T} \right)_{int rev}$$

Total entropy (S) is an extensive property with units J/K, and entropy (s) is intensive with units J/kg-K.

The change in entropy for a process is

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{int rev}$$

Entropy is a property, and like all other properties, it has fixed values at fixed states. Therefore, the entropy change ΔS between two specified states is the same no matter what path, reversible or irreversible, is followed during a process.

For an isothermal process

$$\Delta S = \frac{Q}{T_0}$$

7.2 The Increase of Entropy Principle 334

For an irreversible process, the change in entropy is

$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

Which in differential form becomes

$$dS \geq \frac{\delta Q}{T}$$

Meaning that entropy is constant for a reversible process and increasing for an irreversible process. The entropy change for a process with entropy generation is

$$\Delta S_{sys} = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

Where S_{gen} is always positive (or zero for a reversible process). This can be summed up by the increase in entropy principle. Entropy of an isolated system never decreases. It is constant for a reversible process and increases for a process with irreversibilities.

$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

The inequality is always = for reversible and > for irreversible processes.

These equations allow for some conclusions to be drawn:

- Processes have a certain direction. A process cannot go in a direction which violates the increase in entropy principle
- Entropy is **not** conserved
- Entropy generation is a measure of performance degradation since it is a direct result of irreversibility
- Equilibrium of a system occurs when entropy is at its maximum value

7.3 Entropy Change of Pure Substances 337

Entropy changes of pure substances utilize the property tables. For a saturated mixture, the entropy is found from

$$s = s_f + x s_{fg}$$

Where x is the quality

$$x = \frac{v - v_f}{v_{fg}}$$

And the change in total entropy is

$$\Delta S = m(s_2 - s_1)$$

7.4 Isentropic Processes 340

An isentropic process is adiabatic and internally reversible. This means that

$$\Delta S = 0$$

An adiabatic and internally reversible process is always isentropic, but there are isentropic processes which are not adiabatic or reversible (heat loss offsets entropy gain due to irreversibility) but this is not what is typically meant by an isentropic process.

Many engineering systems can reasonably be approximated as isentropic since irreversibility is low and they are nearly adiabatic (this is very common in aerospace engineering, such as with aerodynamic calculations)

7.5 Property Diagrams Involving Entropy 342

Two common diagrams used in thermodynamics are the T-S diagram and h-s diagram. These are used to visualize thermodynamic processes in relation to the second law. The T-S plot is based on the equation

$$\delta Q_{int\ rev} = T dS$$

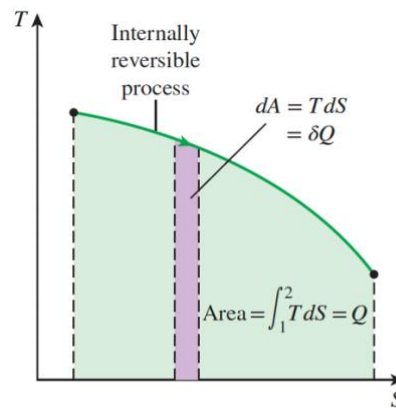


FIGURE 7-16

On a T-S diagram, the area under the process curve represents the heat transfer for internally reversible processes.

And the enthalpy-entropy diagram (also called a Mollier diagram) is typically used for steady-flow systems like nozzles, turbines, and compressors.

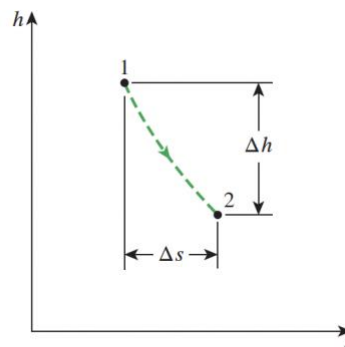


FIGURE 7-18

For adiabatic steady-flow devices, the vertical distance Δh on an h-s diagram is a measure of work, and the horizontal distance Δs is a measure of irreversibilities.

7.6 What is Entropy 343

Entropy is a measure of *disorder*. It can be thought of as molecular randomness. Entropy increases as the position of molecules in a system becomes more random and unpredictable. This is why entropy is lower in a solid than in a gas.

Entropy is the big focus of statistical thermodynamics, which looks at all the possible microstates of a system and probabilities of those states existing. Even though a system is in equilibrium when looking at it macroscopically, there are many different possible states that can exist when looking at the system microscopically. Boltzmann and Gibbs devised probabilistic relations which takes the probabilities of those microstates to calculate the entropy of the system.

Since entropy is a measure of molecular random movement and lack of predictable arrangement, the entropy of a pure crystalline structure of a substance at absolute zero is zero. This is known as the third law of thermodynamics and is the reference point for entropy in a system.

Entropy is also a measure of “wasted” energy, in the sense that entropy cannot be converted to work. Think of a paddle wheel in still air. Even though the individual molecules in the air have kinetic energy, the wheel will not turn without organizing that energy. Once that energy is organized, however, there is no entropy transfer when energy transfer is converted to work. Turning a frictionless shaft does not produce entropy, for example.

Quality of energy is inversely related to entropy, and heat is essentially a form of disorganized energy.

7.7 The T ds Relations 347

The definition of entropy is simple when T is constant, but for a varying temperature, a relationship between δQ and T must be formed. Using conservation of energy and the definition of entropy, Gibbs derived the following equation (the first Gibbs equation)

$$Tds = du + Pdv$$

And using the definition of enthalpy, the second equation is

$$Tds = dh - vdP$$

Even though these equations were derived using a reversible process, they hold for any thermodynamic process.

7.8 Entropy Change of Liquids and Solids 349

The Gibbs equation can be simplified since these states of matter are (nearly) incompressible, and $c_p = c_v = c$

$$ds = \frac{c dT}{T}$$

With the integral form

$$s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} = c_{avg} \ln \left(\frac{T_2}{T_1} \right)$$

7.9 The Entropy Change of Ideal Gases 352

Using the Gibbs equations and the equation of state, the following equation can be used to find the differential entropy change

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

And an alternate form

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

With the integral forms

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \left(\frac{v_2}{v_1} \right)$$

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \left(\frac{P_2}{P_1} \right)$$

There are two possible approaches to solving these, an approximate approach, and an exact approach. The approximate approach uses the average specific heat between the initial and final state.

$$s_2 - s_1 = c_{v,avg} \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$$

$$s_2 - s_1 = c_{p,avg} \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

The exact approach requires finding reference entropy values at each temperature.

$$s^\circ = \int_0^T c_p(T) \frac{dT}{T}$$

This definition can be used to find the exact entropy change

$$s_2^\circ - s_1^\circ = \int_1^2 c_p(T) \frac{dT}{T}$$

$$s_2 - s_1 = s_2^\circ - s_1^\circ + R \ln \left(\frac{v_2}{v_1} \right)$$

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R \ln \left(\frac{P_2}{P_1} \right)$$

The isentropic relations can be derived by setting $s_2=s_1$ and solving. The approximate solution yields

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1} \right)^{\gamma-1} = \left(\frac{P_2}{P_1} \right)^{1/\gamma}$$

where γ is the ratio of specific heats

$$\gamma = \frac{c_p}{c_v}$$

Also recall that the gas constant R is defined as

$$R = c_p - c_v$$

Relative pressure is defined as a dimensionless quantity to use for optimization calculations

$$\frac{P_2}{P_1} = \frac{e^{s_2^\circ/R}}{e^{s_1^\circ/R}}$$

$$\left(\frac{P_2}{P_1} \right)_{s=const} = \frac{P_{r2}}{P_{r1}}$$

Relative specific volume is also a dimensionless quantity

$$\left(\frac{v_2}{v_1} \right)_{s=const} = \frac{v_{r2}}{v_{r1}}$$

These relative values are typically tabulated and used for calculating final temperatures of isentropic processes